

Victor Talrose: An Appreciation

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Last year, in Moscow, we celebrated the 75th birthday of Professor Victor Talrose. At this age, he is still an active scientist, full of new ideas. During this Jubilee celebration, Professor Talrose received numerous messages of congratulation from his colleagues, many of them from abroad. As a member of the Organizing Committee for his Jubilee celebration, I was involved in correspondence with these colleagues. It was a great honor for me to be involved in this celebration and now to be asked to make some comments, as a postscript to the celebration, on the work and career of Victor Talrose. The first well known work of Talrose¹ was selected by the Editors of this Journal as being one of the pivotal papers of the century in mass spectrometry. This publication started the world-wide interest in ion–molecule reactions during the 1950s, an interest which has grown into a large research area in the subsequent decades. This field has provided a huge amount of information about the structure and reactivity of ions and launched the powerful method of analysis known as chemical ionization.

The aim of this contribution, in common with the overall aim of this series of Historical Feature articles, is to remind the younger generation of mass spectrometrists of the origins of the field of organic ion–molecule reactions in the gas phase. This is a little difficult to do, since Ref. 1 was originally published in Russian, in the *Reports of the Soviet Academy of Sciences*. Although this journal is translated into English, few libraries have these translations, so much so that there are many references to this paper but clearly few authors who make this citation do so on the basis of having read it. For these reasons, we thought it pertinent to retranslate Ref. 1, the most often cited of Talrose's papers, and to make some comments of a scientific, personal and historic character. This is an appropriate time to recognize the many achievements of Professor Talrose, as well as those of some of his co-workers in the Institute of Energy Problems of Chemical Physics and other Russian research institutions.

During his scientific career, which has coincided with the Golden Age of Soviet Science, Victor worked in many fields of science and made contributions, not only to mass spectrometry, but also to other fields of modern

chemical, physical, forensic and military science. He was awarded the Lenin Prize, the highest Prize in the former Soviet Union, for a series of papers in the field of chemical lasers. Abroad, Victor is known as an outstanding specialist in the field of mass spectrometry, as demonstrated by the many warm letters he received from his international colleagues in this subject.

Talrose started his scientific career in the Institute of Chemical Physics of the Soviet Academy of Sciences in 1946. Many years later in 1987 he organized his own Institute of Energy Problems of Chemical Physics. He came to the Institute of Chemical Physics after graduating from the Department of Chemistry of Moscow State University. His graduation was delayed by service in the Second World War in Germany, for which he volunteered as a second-year university student. He returned to the University after being seriously wounded. In this he can be thought lucky because only 2% of Russian fighting men of his age came back from the war.

Reference 1 was the second paper of the young Minor Scientific Worker (the lowest rank position of scientific workers in the Soviet Academy of Sciences). His first paper² was published with a prominent Russian academician, Voevodskii, well known for his pioneering work in the application of electron spin resonance to chemistry. In this first study, published in 1947, Talrose determined the activation energy for the process $H + O_2 \rightarrow OH + O$ by measuring ignition temperature limits for the hydrogen–oxygen mixture. This paper is well known to specialists in combustion and this mixture of fuels is widely used in modern jet technology.

The head of the laboratory where Talrose started his research career was another prominent Soviet academician, Kondrat'ev. He was a close colleague of the Director of the Institute, Nobel Prize winner Academician Nikolay Nikolaevich Semenov. Kondrat'ev's main interest was in the field of elementary processes and, especially, the elementary processes involved in radical reactions with molecules. He was thus interested in mass spectrometry as a potential method for the investigation of the reactions of free radicals. Before the Second World War, when the Institute of Chemical Physics was located in Leningrad, Kondrat'ev performed some experiments with his colleagues, J. Eltenton and B. Vasil'ev, on the formation of N_2H^+ and COH^+ in the course of ionization of mixtures of hydrogen with nitrogen and carbon oxide, respectively. Kondrat'ev decided to continue these investigations at a

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new level when the Institute moved from Leningrad to Moscow after a short-term evacuation of Kazan' during the war. In Moscow, Kondrat'ev decided to create a mass spectrometry group as a base to investigate radical processes. These studies were started in 1950 by Talrose and his first pupil, Anna Konstantinovna Ljubimova, who worked with Victor until her retirement. They started their studies into the electron ionization (EI) of hydrocarbons. The vacuum system they used on the home-made 90° sector mass spectrometer, was very poor from a contemporary point of view—the experiments turned out to be run in the pressure region which corresponds, in modern terms, to chemical ionization conditions. (Parenthetically, the term 'chemical ionization' was later introduced into the mass spectrometry literature by Field and Munson.³ However, the term is not completely adequate and fails to distinguish real chemical ionization, in which neutral particles become ionized as a result of chemical reaction(s), from these ion–molecule processes. The ASMS nomenclature⁴ recommends the term 'chemi-ionization' for this latter process. In our laboratory, it was forbidden to use the term chemical ionization for ion–molecule reactions at high pressure. Instead, it was recommended to use ion–molecular reaction ionization, a little longer term but a more appropriate one.)

The strangest thing Viktor and Anna saw in their experiments was an ion corresponding to mass 17 u in the mass spectrum of methane under these conditions. Without hesitation, they assigned this peak to the ion of CH_5^+ and called it 'methonium.' Note that their experiment was not the first attempt to obtain the mass spectrum of methane at low pressure. The first was made by J. J. Thomson. If one takes a look at the mass spectrum Thomson measured,⁵ one can see a pronounced signal at mass 17 u. Thomson appears not to have interpreted this peak: it seems to have taken someone of Victor Talrose's temperament to make, without any hesitation, an assignment which contradicted the strict valence rules well established by this time. Both objective and subjective factors played a role in this interpretation. As an objective factor, we can attribute Kondrat'ev's observation of proton attachment to N_2 and CO and also the existence of H_3^+ , observed by Thomson in 1912. An evident analogy was offered, since if the proton can stick to H_2 , N_2 and CO, why can it not stick to methane? As a subjective factor, besides the great wish of a young scientist to discover something unusual, support was offered the idea by Kondrat'ev, who was then the most prominent professional in questions of structure and elementary processes in the Soviet Union. Of course Kondrat'ev must have known of Hückel's paper,⁶ in which he came to the conclusion that electron pair delocalization over more than two atoms is possible.

Reaction to the publication of Ref. 1 from the organic chemistry community was unanimous: the finding was judged impossible because it contradicted valency rules. This judgement came despite the fact that at approximately the same time what is now called hypervalency was observed in the bulk phase is diboranes⁷ and bridged norbornyl cations.⁸ Later, the chemistry of hypervalent compounds became a very hot research field. To convince themselves and colleagues that the

peak at mass 17 u was nothing else but CH_5^+ , Talrose resolved the multiplet of mass 17 u using a mass spectrometer with the best resolution available at that time.⁹ These experiments were carried out in the Kapica Institute of Physical Problems, which was and is still the nearest neighbor of the Institute of Chemical Physics, and presented in *Reports of the Soviet Academy of Sciences* by the world famous theoretical physicist and Academician, Lev Landau.

Talrose and Lubimova did not observe the formation of hypervalent protonated ions in the EI mass spectra of other alkanes. Later, it was found that these protonated ions are formed but only at lower temperatures.¹⁰ The other new and exciting thing they did observe was the unexpected absence of an activation energy in the ion–molecule reactions they investigated. Later, Talrose and his best pupil, Evgenij Frankevich, checked this peculiarity on the broad number of compounds (70 reactions).¹¹ Frankevich is now a Professor at the Moscow Institute of Physics and Technology (organized by Josef Stalin in 1947 as an élite university to prepare specialists in different fields of modern science and technology, especially nuclear physics and space research) who is actively working in the field of photochemistry and photophysics of organic semiconductors. He discovered the 'Frankevich effect,' which describes the influence of a magnetic field on luminescence in solid organics. He was awarded the Lenin Prize for the cycle of papers on spin effects in organic semiconductors. By thorough investigation of the energetics of reactions using Berry's method¹² of ion deflection, Talrose and Frankevich found that an exothermic ion–molecule reaction does not require that the partners have relative kinetic energy. Even now it is not completely understood why the presence of the charge in the reacting system so drastically changes the reactivity, even in isoelectronic systems. The discovery that ion–molecule reactions, if exothermic, always occur, whereas if endothermic, they do not occur, permitted Talrose and Frankevich to invent the method of proton affinity determination¹³ using, as they called it, the 'fork method' (now known as the bracketing method). The proton affinity values they obtained for some molecules (e.g. water) are still included in modern proton affinity databases. Continuing to work in this newly opened field, Talrose and Frankevich in 1960 introduced the pulsed method of measuring rate constants of ion–molecule reactions,¹⁴ a method which was to be accepted later by many laboratories working in this field. The first reaction investigated by this method was, not surprisingly, $\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$.

The main goal of Kondrat'ev, the creation of a mass spectrometry facility for investigation of radical reactions, was achieved only in the later 1960s. Talrose built an instrument capable of separating and focusing radicals and collided them with molecules and detected radical and molecular products in different electronically and vibronically excited states. In this work he used low-energy electrons for the ionization (so-called soft ionization technique) and mass spectrometric detection methods. Pioneering work in the field of mass spectrometry of free radicals was done using this instrument. At least three generations of mass spectrometrists subsequently used this instrument. The main contribu-

tions were made by Alexander Dodonov, best known for the invention of the orthogonal TOF-ESI combination, an instrumental arrangement currently enjoying great success. The free radical mass spectrometer is still in use by Professor Igor Morozov in investigations of night-time atmospheric radical processes responsible for ozone destruction.

The chemistry of free radicals became one of the main fields of Talrose's interest. He organized and headed a Department of Free Radicals (later renamed the Department of Physical Method of Stimulation of Chemical Processes) of the Institute of Chemical Physics, which was well equipped for that time, with a centerpiece linear accelerator from the Kaiser Wilhelm Institute of Physics in Germany, a Co-60 source and

many EPR and mass spectrometers. Numerous investigations in fundamental and applied radiation chemistry were carried out in this Department. It was one of the best bases of the legendary Fiztech, the elite educational system organized in such a way that students starting from the third year work in the laboratories of one of the Academy of Science Research Institutes as a so-called base institute. The Department of Chemical and Molecular Physics was headed for nearly 20 years by Professor Talrose. He continues to work there as leader of a research group. Now hundreds of his pupils are spread around the world, continuing to work in directions he discovered. His enthusiasm and faith will always represent to us a standard of how to serve science.

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